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Kahle

March 27, 2002

Functionalized Polyurethane

The present invention relates to a new, water-dilutable polyurethane, as well as its use in series painting of automobiles.

It is known to use polyurethane as a binder for high-grade coating compositions. The resulting coatings have excellent mechanical properties, especially with respect to the ability of the cured paint film to bear stress.

Polyurethanes are therefore often used in the production of ordinary car-paint layers.

Such a car-paint layer generally consists of a total of four different layers (four-coat structure). These four layers are applied in succession in separate painting units.

The first layer is situated directly on the sheet metal of the car, is an electrophoretically applied layer (electrocoat layer, KTL layer), which is applied by electrocoat dip coating (mostly a cathodic dip coating (KTL)) for corrosion protection and then stoved.

The second layer, about 30 to 40 μm thick, situated on the electrocoat layer, is a so-called extender layer, which, on the one hand, offers protection against mechanical attack (stone-impact protection function) and, on the other hand, assures adequate quality of the topcoat, i.e., smoothes the rough surface of the crude car body for subsequent finishing and fills in smaller unevennesses. The paints used to produce this extender layer also contain pigment in addition to binders. The wettability of the pigments used then has an effect on the quality of the topcoat of the entire multilayer coating and also on the gloss of the extender, as is required by some automakers. The extender layer is mostly produced by application with electrostatic high-rotation bells and then a stoving process at temperatures above 130 °C.

The third layer, situated on the extender layer is the base coat, which gives the car body the desired color by appropriate pigments. The base coat is applied in ordinary spray methods. The layer thickness of this ordinary base coat, depending on the color, is between about 12 and 25 μm . This layer, especially in metallic-effect paints, is generally applied in two process steps. In a first step, it is applied by electrostatic high-rotation bells, followed by a second application with pneumatic atomization. This layer is dried (when an aqueous base coat is used) with infrared radiators and/or hot-air convection.

The fourth and uppermost layer, situated on the base coat, is the clear coat, which is generally applied in one application by electrostatic high-rotation bells. It imparts the desired gloss to the car body and protects the base coat from environmental effects (UV radiation, salt water, etc.).

The base coat and clear coat are then stoved together.

The extenders used to produce a multilayer coating for the automotive industry are still always based to a significant percentage on solvents, and reach solid concentrations of up to 60%. This high solid concentration assures efficient application and therefore good quality of the top coat of the multilayered coating. Examples of such conventional extenders are known from DE 33 37 394 A1.

The stoving temperatures are generally between 155 and 165 °C. A so-called "overstoving stability" of up to 190 °C is also required by some automakers. This means that mechanical properties, such as adhesion and stoning resistance, must not significantly deteriorate under these high stoving conditions. In order to satisfy this requirement, the binder compositions of appropriate extender systems often consist of saturated polyesters combined with highly alkylated melamine resins as crosslinking agents. Combinations with polyurethanes are also known, especially with blocked polyisocyanates. The blocking agent most commonly used for this purpose is methylethyl ketoxime. The advantages of using methylethyl ketoxime over other blocking agents consist of its favorable deblocking temperature, its volatility, and its good availability. A shortcoming is its yellowing tendency, which sharply restricts applicability for light stoving paints.

Crosslinking with blocked polyisocyanates does improve stoning resistance and oversteoving stability, but co-use of melamine resins as a crosslinking agent is unavoidable with respect to other important properties of the extender layer, such as good grindability, resistance to chemical attack, for example, resistance to brake fluid. Moreover, the flow and quality of the topcoat are positively influenced by a combination of these two crosslinking agents.

Such hybrid systems of blocked polyisocyanate and melamine resins, however, are problematical with respect to proper adjustment of their reactivity: whereas the deblocking reaction in polyurethanes and subsequent urethane formation reaction are supported with basic catalysts, the crosslinking reaction of melamine resins can only be accelerated with acid catalysts. Mutual negative effects are unavoidable.

Against the background of solvents used in conventional extenders and the environmental problems related to them, developments have intensified in the field of water-dilutable extenders based on polyurethanes.

In order to achieve water dispersibility of polyurethanes, carboxyl groups are incorporated in the molecule, which (often at the end of the synthesis process) are converted with amines (preferably volatile) to carboxylate anions by neutralization. This incorporation of carboxyl groups very often occurs by conversion with dimethylol-propionic acid.

Examples of such water-dilutable extenders that contain appropriate polyurethanes are known from EP 0,726,919 A1, EP 0,594,685 B1, EP 1,110,983 A2, and EP 1,110,987 A1.

Polyurethanes with blocked isocyanate groups are also disclosed in DE 199 30 555 C1, which are obtained using alkanolamines as chain extenders. During chain extension, the hydroxyl groups of the alkanolamine react with the NCO groups of the polyisocyanate to form a urethane bond.

Water dispersibility of the polyurethanes produced is also achieved here with incorporated carboxyl groups by conversion with dimethylol-propionic acid and subsequent neutralization.

However, it has been found that only a solid concentration of up to about 50% can be achieved on an industrial scale with these water-dilutable extender compositions based on polyurethane. In

comparison with conventional extenders, this difference causes limited application reliability and clearly visible deteriorations in the resulting multilayer coating, especially with respect to top-coat condition.

Against the background of additional energy savings and shortening of the process steps, there is also a requirement in the automotive industry to demand a reduction in extender stoving temperature from the present 160 °C. However, such extenders must still have an overstoving stability to 190 °C.

A reduction in stoving temperature by increasing the reactivity of corresponding extender systems, for example, by using more highly reactive melamine resins, leads to embrittlement under overstoving conditions, which results in a total loss of stone-impact protection.

A reduction of melamine-resin content would have the drawback that the resistance to chemical attack (for example, by brake fluid) is adversely affected.

An adequate stone-impact protection function of a multilayer coating in the field of automotive series painting exists when the conditions of both "the mono-impact test" and the "multi-impact test" are met.

In the so-called "mono-impact test," a fracture in the structure of the multilayer coating is localized under the influence of a precisely defined mechanical load. In the so-called "multi-impact test," the mechanical stressability of a larger surface of the top coat is simulated under different mechanical loads. Additional details of both tests are found in the examples.

The task of the present invention is to provide a polyurethane that can be used for the production of water-dilutable extender compositions with a solid content of more than 50 wt%, especially more than 55 wt%, in multilayer coating of car bodies, whereby these water-dilutable extender compositions lead to resulting extender layers, already at a stoving temperature of 140 °C, that have both the stoning resistance required by the automotive industry and also overstoving stability.

The resulting multilayer coating should also have no deterioration in properties with respect to the overall property level in comparison with those of the state of the art, especially with respect

to application reliability and yellowing resistance of the extender layer, as well as the quality of the top coat of the overall structure.

This task is solved according to the invention by a water-dilutable polyurethane with at least two free OH groups, obtained from a first conversion of a primary and/or secondary alkanolamine with an NCO compound to an intermediate, followed by addition of a cyclic carboxylic-acid anhydride to the intermediate; whereby

- the NCO compound has at least one free NCO group and no blocked NCO group;
- during the first conversion to the intermediate, all the alkanolamine is converted, so that the nitrogen atom of the alkanolamine reacts with one of the free NCO groups of the prepolymer to form a urea bond; and
- the cyclic carboxylic-acid anhydride reacts with the OH group of the intermediate originating from the alkanolamine, with ring opening.

In principle, all known isocyanates can be used as the NCO compound. For the selection of this NCO compound, it is only critical that these isocyanates produce products after conversion with the alkanolamine that are soluble in solvents inert with respect to isocyanates or in the melt and are therefore accessible to subsequent reaction with the cyclic carboxylic-acid anhydride.

In view of simpler synthesis it is advantageous that the NCO compound has no OH group.

The NCO compound is converted in the second process step by conversion with at least one alkanolamine to a functionalized polyurethane/urea compound. With respect to the first conversion to the intermediate it should be noted that the term "all the alkanolamine" is understood to mean that the alkanolamine is converted so that in the reaction mixture containing the intermediates, a content of free alkanolamine of less than 0.5 wt% is present, with respect to the solid content of the resin.

Conversion of the initial components then occurs according to well known methods of organic chemistry (cf., for example, *Kunststoff-Handbuch* [Plastics Handbook], vol. 7: Polyurethanes, edited by Dr. Y. Oertel, Carl Hanser Verlag, Munich, Vienna, 1983).

The conversion is optionally conducted in the presence of volatile solvents miscible with water that are inert with respect to isocyanates. Methyl ethyl ketone and/or acetone are preferably used.

In order to achieve dispersibility in an aqueous medium, at least one cyclic carboxylic-acid anhydride is added to the hydroxyl groups originating from the alkanolamine, with ring opening. The amount of cyclic carboxylic-acid anhydride should be chosen so that the resulting acid number lies between 10 and 50, preferably between 20 and 30.

The polyurethane so obtained is converted to an aqueous dispersion occurs by neutralization of the carboxyl groups with amine and/or amino alcohols. Examples of appropriate compounds are ammonia, tertiary amines such as trimethylamine, triethylamine and/or amino alcohols such as dimethyl ethanolamine, diethylethanolamine, methyldiethanolamine, and triethanolamine. Neutralization can occur in the organic phase or in the aqueous phase. Dimethylethanolamine is preferably used as a neutralizing agent.

The water-dilutable polyurethane so produced is characterized in that it can be used in water-dilutable extender compositions in multilayer coating in the automotive industry that have a solid concentration of more than 50%. Using ordinary crosslinking agents, layers that have both the stone-impact resistance required by the automotive industry and excellent overstoving stability result from extender compositions containing the polyurethane according to the invention already at a stoving temperature of 140 °C.

As the examples show, the resulting multilayer coatings do show no deterioration in properties in comparison with ordinary multilayer coatings of the state of the art, but they also show excellent features simultaneously with respect to application reliability and yellowing resistance of the extender layer and the quality of the topcoat of the overall structure.

In order to support water dispersibility, it can be advantageous to modify this NCO compound before conversion with nonionic, stabilizing groups. Alkoxypoly(oxyalkylene) alcohols are particularly preferred for this purpose. Particularly suitable alkoxypoly(oxyalkylene) alcohols are chosen from the group of monoalkylated polyethylene oxides, as marketed under the trade name PLURIOL® A from the BASF company.

According to a preferred variant of the present invention, a polymer is used as the NCO compound that is obtained by conversion of at least one polyol with at least one polyisocyanate to an isocyanate group-containing a polyurethane prepolymer. Examples of appropriate polyols are saturated or olefinically unsaturated polyester polyols and/or polyether polyols with an average molecular weight of 100 to 5000, preferably 500 to 2000. Small amounts of a carboxyfunctional polyol can also be used.

By choosing appropriate initial compounds for this prepolymer, the physical and technical properties of the resulting multilayer coating can be adjusted accordingly.

The NCO compound can preferably have two free NCO groups. A narrower molecular-weight distribution is achieved thereby, in comparison with polyfunctional compounds.

All appropriate compounds can be used as the alkanolamine. It should be noted that the alkanolamines used according to the invention have a hydrogen atom bonded to the nitrogen atom. These include 1-amino-3-propanol, 1-amino-2-propanol (isopropanolamine), 1-amino-4-butanol, 1-amino-5-pentanol, 1,1'-iminodi-2-propanol (diisopropanolamine), and/or 2-(2-aminoethoxy)ethanol.

Tertiary alkanolamines are not to be used according to the present invention.

Alkanolamines in which at least one OH group of the alkanolamine is bonded to the nitrogen atom through a substituted or unsubstituted alkyl group with 2 to 6 carbon atoms in the main chain are preferably used.

Examples include aminobutanol, 1-amino-5-pentanol, aminohexanol, 2-(2-aminoethoxy)ethanol, isopropanolamine, diisopropanolamine, 2-amino-2-methyl-1-propanol, and 2-amino-2-methyl-1,3-propanediol.

In particular, the OH groups originating from the alkanolamine can be fully or partially secondary. Examples of such compounds are isopropanolamine and diisopropanolamine. Other alkanolamines with primary OH groups can also be used, such as N-(2-aminoethyl)ethanolamine and/or butylethanolamine.

Diethanolamine and/or diisopropanolamine are used with particular preference as the alkanolamine for producing the polyurethane according to the invention.

With respect to the sufficient water dispersibility, the polyurethane of the present invention should have an acid number of at least 10 mg KOH/g, especially at least 20 mg KOH/g.

The average molecular weight of the polyurethane according to the invention is preferably between 500 and 10,000, especially between 1000 and 4000.

The cyclic carboxylic-acid anhydride can be chosen from the group of phthalic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, methyl-hexahydrophthalic anhydride, succinic anhydride, and maleic anhydride.

Trimellitic-acid anhydride is used with particular preference as the cyclic carboxylic-acid anhydride.

According to another object of the present invention, likewise claimed, the water-dilutable polyurethane just described is used in combination with a melamine resin to produce heat-curable coating compositions. In principle, all appropriate crosslinking agents can be used for this purpose.

Highly alkylated melamine resins that are compatible with the polyurethane according to the invention are particularly preferred. Melamine resins without NH groups are particularly preferred for this purpose, especially hexamethoxymethyl melamine (HMMA).

Such coating compositions can be crosslinked at a temperature of more than 180 °C, which shows sufficient overstoving stability according to the present application.

If overstoving stability is not required for application of a coating composition containing the polyurethane according to the invention, highly reactive melamine resins can also be used to reduce the stoving temperature below 140 °C. Such highly reactive melamine resins are marketed, for example, by the BASF company under the name LUWIPAL® 062.

The water-dilutable polyurethanes just described are used, in particular, to produce coating compositions in the automotive industry, especially extender compositions.

The extender layers are generally applied by spray coating, for example, by compressed air, hot or airless spraying, or by electrostatic coating methods, for example, high-speed bells (minibells), electrostatic automatic or hand spray guns with air support, or by rollers, for example, in a belt coating method.

The following examples will explain the invention without it being restricted to them.

Example 1:

Preparation of a polyurethane according to the invention:

Preparation of a polyester diol (A):

The following starting products were weighed into a glass flask with a volume of 4 liters, equipped with an agitator, a packed column, and a reflux condenser, as well as temperature measurement for the reaction mixture and the top of the column: 1730 g 1,6-hexanediol and 1622 g isophthalic acid. The reaction mixture was melted at a temperature of 120 °C, and then the reaction temperature raised over 4 hours to 230 °C under agitation. The temperature rise was controlled by measuring the overhead temperature of the packed column. The overhead temperature was then limited to maximum of 99 °C. The melt was condensed for 12 hours at a temperature of 230 °C, until the acid number dropped to a value of 2 mg KOH per of solid resin. The reaction product was then kept at a temperature of 180 °C for an hour under vacuum. The average molecular weight was 614 g/mol.

Preparation of the polyurethane dispersion:

850.0 g of polyester diol (A) and 409.8 g isophorone diisocyanate, 839.8 g methylethyl ketone, and 2.0 g dibutyl tin dilaurate were introduced to a glass flask with a volume of 4 liters equipped with an agitator, a reflux condenser, and temperature measurement and heated under agitation at 80 °C, and the reaction continued until the NCO content reached a constant value. The resin solution was then cooled to 40 °C and 96.9 g diethanolamine was added. The mole ratio of isocyanate to diethanolamine for this example was 1:1. After a decline of the exothermic reaction, the temperature was increased over a half hour to 80 °C. A half hour after reaching this temperature, 57.6 g trimellitic anhydride was added. After a reaction time of 1 hour, 53.4 g dimethyl ethanolamine and 2766.4 g deionized water were introduced, during which the

temperature did not drop below 60 °C. After eliminating methylethyl ketone under vacuum, a stable opaque dispersion with a solid concentration of 43% was obtained.

Example 2:

Preparation of a polyurethane according to the invention:

Preparation of a polyester diol (B):

The following starting products were weighed into a glass flask with a volume of 4 liters equipped with an agitator, a water separator, and a reflux condenser, as well as temperature measurement for the reaction mixture: 1918.8 g 2,2-bis-[p-(β -hydroxytriethoxy)phenyl] propane, 431.6 g isophthalic acid, and 200 g xylene. The reaction mixture was raised to a reaction temperature of 180 °C over 2 hours during agitation. It was raised 10 C° per hour to 210 °C. The melt was then condensed for 12 hours at a temperature of 230 °C, until the acid number had dropped to a value of 2 mg KOH/g. The reaction product was then kept under vacuum for an hour at a temperature of 180 °C. The average molecular weight was 1736 g/mol.

Preparation of the polyurethane dispersion:

1041.6 g polyester diol (B) as well as 266.4 g isophorone diisocyanate, 872 g methylethyl ketone, and 2.0 g dibutyltin dilaurate were introduced to a glass flask with a volume of 4 liters equipped with an agitator, a reflux condenser, and temperature measurement and heated under agitation to 80 °C, and the reaction continued until the NCO content had reached a constant value. The resin solution was then cooled to 40 °C, and 94.4 g diethanolamine was added. The mole ratio of isocyanate to diethanolamine for this example was 1 to 0.75. After a decline of the exothermic reaction, the temperature was raised over half an hour to 80 °C. A half hour after reaching a temperature, 57.6 g trimellitic anhydride was added. After a reaction time of an hour, 53.4 g dimethyl ethanolamine and 1858.2 g deionized water were introduced, during which the temperature did not drop below 60°C. After eliminating methylethyl ketone under vacuum, a stable opaque dispersion with a solid concentration of 45% was obtained.

Example 3.1: Preparation of a pigment paste:

The following components were weighed in the sequence mentioned into a stirred stainless-steel

vessel and homogenized by agitation after each addition: 443.6 g of the polyurethane dispersion from example 1, 7.7 g Surfynol 104E (wetting and dispersing additive), 15.7 g Additol XL 250, 13.0 g Drewplus, 7.7 g Aerosil R 972 (Degussa), 433 g barium sulfate (Blanc Fixe[®] micro), 49.5 g titanium dioxide (Tiona RCL 628), 23.5 g Printex G, 26 g talc IT extra, and 66.7 g deionized water. The mixture was predispersed over 30 minutes in a dissolver and then ground in a sand mill to a particle fineness of <10 µm. The temperature was kept below 40 °C during the grinding process.

Example 3.2: Preparation of a pigment paste:

The following components were weighed in the sequence mentioned into a stirred stainless-steel vessel and homogenized by agitation after each addition: 423.8 g of the polyurethane dispersion from example 2, 7.7 g Surfynol 104E (wetting and dispersing additive), 15.7 g Additol XL 250, 13.0 g Drewplus, 7.7 g Aerosil R 972 (Degussa), 433 g barium sulfate (Blanc Fixe[®] micro), 49.5 g titanium dioxide (Tiona RCL 628), 23.5 g Printex G, 26 g talc IT extra, and 86.5 g deionized water. The mixture was predispersed over 30 minutes in a dissolver and then ground to a particle fineness of <10 µm in a sand mill. The temperature was kept below 40 °C during the grinding process.

Example 4.1: Preparation of an extender formulation according to the invention:

The extender was prepared by mixing 523 g of pigment paste according to example 3.1 and 343 g of the polyurethane dispersion from example 1 with 122.4 g of a highly alkylated low-molecular-weight melamine resin etherified with methanol, 26 g N-methyl pyrrolidone, and 13 g of an aliphatic hydrocarbon mixture with boiling points of 180 °C and 210 °C, as well as 6.5 g BYK 381 (flow-control additive, BYK Chemie). The viscosity was set with deionized water at 120 mPas at a shear rate of 1000 s⁻¹ with a rotary viscosimeter. The solid concentration was 55%.

Example 4.2: Preparation of an extender formulation according to the invention:

The extender was prepared by mixing 523 g of pigment paste according to example 3.2 and 304.9 g of the polyurethane dispersion from example 2 with 122.4 g of a highly alkylated low-molecular-weight melamine resin etherified with methanol, 26 g N-methyl pyrrolidone, and 13 g of an aliphatic hydrocarbon mixture with boiling points of 180 °C and 210 °C, as well as 6.5 g

BYK 381 (flow-control additive, BYK Chemie). The viscosity was set with deionized water at 125 mPas at a shear rate of 1000 s^{-1} with a rotary viscosimeter. The solid concentration was 54%.

Example 4.3: Preparation of an extender formulation not according to the invention:

Preparation occurred similar to example 4.2, whereby instead of the polyurethane dispersion of example 2, the commercial polyurethane dispersion Resydrol VAZ 6600 from Solutia was used both for the extender composition and for preparation of the pigment paste. The solid concentration obtained was 48% at a viscosity of 125 mPas (shear rate of 1000 s^{-1}).

Application of the extender:

For preparation of the multilayer coating, ordinary and known steel test panels were used, which were coated with a 20- μm thick electrocoat produced from a commercial cationic electrocoat paint.

The test panels were pneumatically coated with the extenders according to the example 4.1, 4.2, and 4.3. The resulting extender layers were predried for 8 minutes at $80\text{ }^{\circ}\text{C}$ and then stoved at $140\text{ }^{\circ}\text{C}$, $160\text{ }^{\circ}\text{C}$ and $190\text{ }^{\circ}\text{C}$ for 20 minutes. An extender with a layer thickness of $35\pm 2\text{ }\mu\text{m}$ was obtained.

A commercial conventional single top coat was pneumatically applied to the extender layer, and after 10 minutes of ventilation at room temperature, it was stoved for 30 minutes at $140\text{ }^{\circ}\text{C}$. The single top coat of the resulting multilayer coating had a layer thickness of $30\text{ }\mu\text{m}$.

The multilayer coatings produced in this way were investigated according to the test described below. The results of the investigations are summarized in the following tables:

The mechanical properties are shown in Table I, whereas Table II shows the effects of overstoving conditions.

Determination of solid concentration:

Solid determination was conducted in a convection furnace by stoving at a temperature of $120\text{ }^{\circ}\text{C}$. For this purpose, 1 g of the substance being tested was applied to a patent cover (diameter 75 mm) distributed uniformly over the surface and dried for an hour in the furnace.

The nonvolatile fraction was then determined by reweighing the cover. A three-fold determination was conducted.

Determination of layer thickness:

The layer thickness was determined using the Surfex instrument from the Phynix Co.

Determination of gloss:

Determination of gloss occurred using the haze gloss instrument of BYK Gardner at angles of 20° and 60°.

Testing for stone-impact resistance (multi-impact test):

Stone-impact resistance was tested using a stone-impact test device according to VDA, model 508, from Erichsen GmbH & Co. KG.

The test sheets were shot at a pressure of 2 bar twice each time with 500 quenched-iron "Diamant" [Diamond] angular shots, size 4-5 mm.

Testing for stone-impact resistance according to BMW (mono-impact test):

The determination was made according to test instruction BMW PA 15063-L of April 1997. A conical test specimen according to VDA test sheet draft 621-428 was then shot at a pressure of 2 bar onto a finished multilayer coating. Chipping and the fracture site in the structure were determined.

Determination of pendulum hardness according to König:

The pendulum hardness was determined with a pendulum-hardness tester from BYK Gardner.

Table I

	Example 4.2 Comparative example according to the invention	Example 4.3 Comparative example not according to the invention
Solid concentration	54%	48%
Quality of top coat*	2	2
Gloss (20°/60°)	78/89	70/90
König hardness (sec) for 160°C	142	149
Stone-impact resistance (VDA)	2	4
BMW chisel (chipping in mm/separation plane)	1/cohesive	3/adhesive

Table II

	Example 4.1 Comparative example according to the invention	Example 4.3 Comparative example not according to the invention
Solid concentration	55%	48%
Quality of top coat*	2	2
Gloss (20°/60°)	69/89	70/90
König hardness (140/160/190°C) sec	124/137/145	84/148/154
Stone-impact resistance VDA (140 °C / 160 °C / 190 °C)	2.5/2.0/2.5	2.5/4.0/4 .5

*Visual evaluation

It can be seen from the values shown in Table I that the extender produced using the crosslinking agent according to the invention has improved properties with respect to solid concentration of the extended formulation ready for application, stone-impact resistance and quality of the top coat of the multilayer coating in comparison with the extenders of the state of the art.

Table II shows that this superiority is also assured under oversteoving conditions.

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Claims

1. A water-dilutable polyurethane with at least two free OH groups obtained from a first conversion of a primary and/or secondary alkanolamine with an NCO compound to an intermediate, followed by addition of a cyclic carboxylic-acid anhydride to the intermediate, in which
 - the NCO compound has at least one free NCO group and no blocked NCO group;
 - during the first conversion to intermediate, all the alkanolamine is converted, so that the nitrogen atom of the alkanolamine reacts with one of the free NCO groups of the prepolymer to form a urea bond; and
 - the cyclic carboxylic-acid anhydride reacts with the OH group of the intermediate originating from the alkanolamine, with ring opening.
2. A water-dilutable polyurethane according to claim 1, characterized in that NCO compound has no OH group.
3. A water-dilutable polyurethane according to claim 1 or 2, characterized in that the NCO compound is modified by at least one alkoxypoly(oxyalkylene) alcohol.
4. A water-dilutable polyurethane according to one of the preceding claims, characterized in that the NCO compound is a prepolymer.
5. A water-dilutable polyurethane according to one of the preceding claims, characterized in that the NCO compound has at least two free NCO groups.
6. A water-dilutable polyurethane according to one of the preceding claims, characterized in that at least one OH group of the alkanolamine is bonded with its nitrogen atom through substituted and unsubstituted alkyl groups with 2 to 6 carbon atoms in the main chain.

7. A water-dilutable polyurethane according to one of the preceding claims, characterized in that the OH groups originating from the alkanolamine are fully or partially secondary.
8. A water-dilutable polyurethane according to one of the preceding claims, characterized in that the alkanolamine is diethanolamine and/or diisopropanolamine.
9. A water-dilutable polyurethane according to one of the preceding claims, characterized in that it has an acid number of at least 10 mg KOH/g, especially at least 20 mg KOH/g.
10. A water-dilutable polyurethane according to one of the preceding claims, characterized in that the polyurethane has an average molecular weight between 500 and 10,000, especially between 1000 and 4000.
11. A water-dilutable polyurethane according to one of the preceding claims, characterized in that the cyclic carboxylic-acid anhydride is chosen from the group of phthalic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, methyl-hexahydrophthalic anhydride, succinic anhydride, and maleic anhydride.
12. A water-dilutable polyurethane according to one of claims 1 through 10, characterized in that the cyclic carboxylic-acid anhydride is trimellitic anhydride.
13. Use of a water-dilutable polyurethane according to one of the preceding claims in combination with a melamine resin to produce heat-curable coating compositions.
14. Use of a water-dilutable polyurethane according to claim 13, characterized in that the melamine resin is a highly alkylated melamine resin.
15. Use according to claim 14, characterized in that the melamine resin is one without NH groups, especially hexamethoxymethyl melamine (HMMA).
16. Use according to one of claims 13 through 15, characterized in that the crosslinking temperature is less than 145 °C.
17. Use according to one of claims 13 to 16, characterized in that the crosslinking temperature is more than 180 °C.

18. Use of a water-dilutable polyurethane according to one of the preceding claims to produce coating compositions, especially extenders in the automotive industry.

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Summary

Water-dilutable polyurethane with at least two free OH groups obtained from a first conversion of a primary and/or secondary alkanolamine with an NCO compound to an intermediate, followed by addition of a cyclic carboxylic acid anhydride to the intermediate, in which

- the NCO compound has at least one free NCO group and no blocked NCO group;
- during the first conversion to the intermediate all the alkanolamine is converted so that the nitrogen atom of the alkanolamine reacts with one of the free NCO groups of the prepolymer to form a urea bond; and
- the cyclic carboxylic acid anhydride reacts under ring opening with the OH group of the intermediate originating from the alkanolamine;

as well as its use to produce heat-curable coating compositions.